Diffusion Experiment and its Isotope Effects of Liquid Lithium due to the TR-IA-6 Rocket

Toshio ITAMI[A,B], Akitoshi MIZUNO[A], Hirokatsu AOKI[A], Minoru KANEKO[C], Tomoharu FUKAZAWA[C], Akira TANJI[D], Yoshihito ARAI[D], Kazumasa GOTO[D], Yukiko YAMAURA[D], Natsumi TATEIWA[D], Masato KOYAMA[E], Tomoji MORITA[E], Haruhiko KAWASAKI[E], Motoi FUJISHIMA[E], Tadahiko MASAKI[F], Shinichi YODA[F], Yukihiro NAKAMURA[G], Naokiyo KOSHIKAWA[G], Tomihisa NAKAMURA[G] and Akio OGISO[G]

Abstract

The diffusion coefficient of liquid lithium, which is expected to show large isotope effects because of its small atomic mass, was measured by the long capillary method under the microgravity due to the launch of the sixth TR-IA rocket. The detailed description is given for the procedure of the microgravity experiments for the very aggressive materials such as liquid lithium. The smaller diffusion coefficient was obtained for ^{7}Li in liquid ^{6}Li compared with the case of ^{6}Li in liquid ^{7}Li. These behaviors were discussed based on the theoretical calculations successfully in a qualitative manner from the point of view of the hard sphere model, in which the hard sphere diameter was determined from the theoretical point of view.

1. Introduction

The space environment has many fascinating properties, such as no gravity, no convection and large vacuum area. For the purpose of diffusion measurements of melts with high melting points, the space has been clarified to be an ideal circumstance[1]. The most advantageous point of it is derived from the absence of gravity, which, on the ground, induces the convection in liquid samples and spoils the concentration profiles of the diffusion experiments. The liquid metals are the most fundamental materials of melts with high melting point. For example, sodium, lithium, liquid iron, copper, aluminum, etc., are directly related to the industrial processes. In addition, from the theoretical points of view, liquid metals has many advantageous points for detailed theoretical analysis, for examples, wide

A Division of Chemistry, Graduate School of Science, Hokkaido University, N10W8, kita-ku, Sapporo 060, Japan (E-mail itami@sci.hokudai.ac.jp)
B Invited Researcher of National Space Development of Agency in Japan (NASDA), 2-1-1 Sengen, Tsukuba, Ibaragi 305, Japan
C Space Department, Ishikawajima Jet Service Co. Ltd., 1-15 Toyosu, 3-Choume, Koto-Ku, Tokyo 135, Japan
D Space Experiment System Developement Department, Ishikawajima-Harima Heavy Industries Co Ltd., 229 Tonogaya, Mizuho-Machi, Nishitama-Gun, Tokyo 190-12, Japan
E Frontiers Joint Research Program Department, Japan space Utilization Promotion Center, 3-30-16 Nishi-Waseda, Shinjyuku-Ku, Tokyo 169, Japan
F Space Utilization Research Center, office of Space Utilization Systems, National Space Development agency of Japan, 2-1-1 Sengen, Tsukuba-Shi, Ibaragi 305, Japan
G Space Experiment Department, National Space Development agency of Japan, 2-1-1 Sengen, Tsukuba-Shi, Ibaragi 305, Japan

Reprinted from J. Jpn. Soc. Microgravity Appl., Vol.16 No.3 (1999) pp.196-206.

liquid ranges, monatomic liquids, the existence of interatomic potentials given by the pseudopotential theories, many techniques for computer simulations, etc. Therefore, it is very interesting to perform microgravity experiments of diffusion of liquid metals, particularly liquid lithium, for which the isotope effect is expected to be found because of its light mass. Unfortunately experiments for liquid lithium is extremely difficult due to aggressive reactivities to many container materials. Therefore it is also very important to develop the experimental method for diffusion experiments under microgravity of liquid lithium. The purpose of this paper is twofold. One purpose is to develop the experimental method under microgravity for aggressive materials like liquid lithium. The other purpose is to investigate the diffusion of liquid lithium under the microgravity of TR-IA-6 rocket.

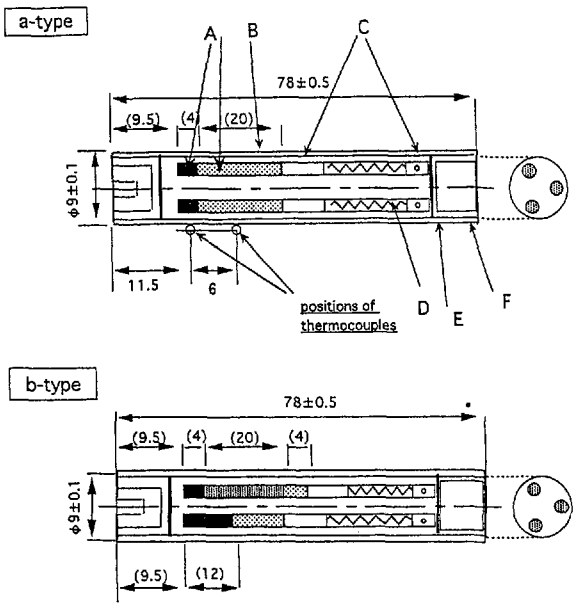

Fig. 1 Cell configurations; A: Sample; B: BN crucible; C: BN plug; D: W spring; E: Cushion material; F: SUS container.

2. Experimental

2.1 Experimental method

In this experiment the self-diffusion coefficient was measured by the long capillary method, whose experimental technique under microgravity has been well established. Four kinds of diffusion experiments at the same time in one flight of TR-IA-6 was performed by employing four furnaces in MPS (Multi Purpose Furnace), which is installed in the TR-IA rocket. MPS is composed of six furnaces whose temperature can be independently controlled. One furnace accommodated one SUS container, into which one BN crucible was inserted. In this BN crucible three holes were drilled for the accommodation of three diffusion samples. In **Fig. 1** is shown the sample cell configuration. As a result 12 pieces of diffusion samples (three pieces x four furnace) were to be thrown into the self-diffusion experiment on the launch of TR-IA-6.

In **Fig. 2** is shown schematically the experimental arrangement of samples. In No. 1 and No. 2 samples of "type a" (MPF-2/a-bu, MPF-3/a-37 and MPF-4/a-20), rods of ^{6}Li (2 mm dia., 4 mm length) were combined respectively with bars of ^{7}Li (2 mm dia., 20 mm length). This arrangement was adopted to try the self-diffusion of tracer ^{6}Li into the liquid ^{7}Li medium. In No. 3 samples of "type a", rods of ^{6}Li were combined respectively with bars of ^{7}Li. This arrangement was adopted to try the self-diffusion of tracer ^{7}Li into the liquid ^{6}Li medium. In "type b" (MPF-5/b-20), No. 1 (No. 3) is planed to measure the self-diffusion of tracer ^{7}Li(^{6}Li) into the liquid ^{6}Li (^{7}Li) medium; No. 2 is the configuration of interdiffusion type of liquid ^{7}Li-^{6}Li alloys. The isotope concentrations of employed stable isotopes are shown in **Tab. 1** together with the natural lithium.

The cell configuration shown in Fig. 1 was determined by considering the reactivity and vapor pressure of lithium and the prevention of Marangoni convection.

The special attentions were paid for the reactivity and vapor pressure of lithium. To prevent lithium samples from oxidation and nitride formation all procedures for the sample preparation were performed in the glove box, as shown in **Fig. 3**. After the enclosure under Ar atmosphere by welding, the SUS containers including lithium diffusion samples could be brought out from the glove box and finally they were brought to Tanegashima Island for the launch of TR-IA-6 rocket. The pressure of Ar was adjusted to be 1 atom at the ex-

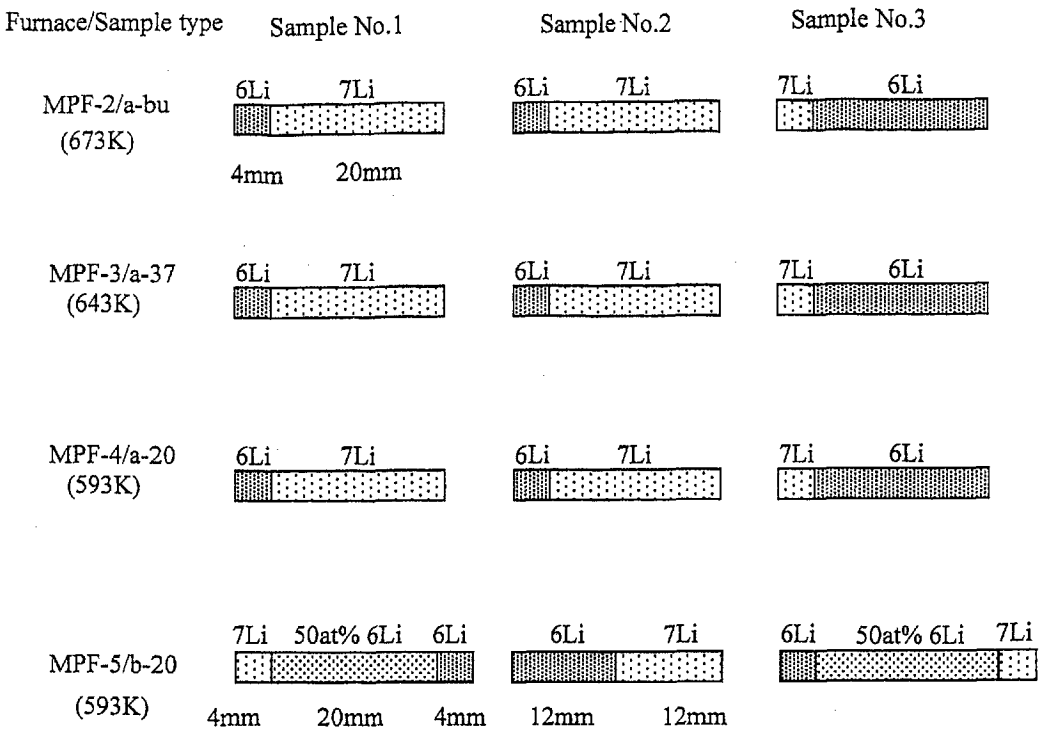

Fig. 2 The configuration of the samples for the sixth of TR-IA rocket experiment.

Tab. 1 The isotopic abundance of Li

	^{7}Li	^{6}Li
Natural Li	92.5 atom%	7.5 atom%
^{7}Li	99.0 atom%	1.0 atom%
^{6}Li	4.38 atom%	95.62 atom%

perimental temperature.

The mother sample bars (^{6}Li, ^{7}Li and 50 at%^{6}Li–50 at%^{7}Li) for the diffusion samples were prepared in the glove box by the casting of melts into the BN mould after the vacuum degassing procedure. Then the diameter of this mother bars were adjusted so that they could be introduced into the three holes in the BN crucible. Required rods and bars with the appropriate length for diffusion experiments were prepared from these mother bars by cutting procedure.

As is well known, the Marangoni convection prevails under microgravity if free surfaces are present in samples. Therefore, for diffusion experiments, the free surface, voids and cavity of samples must be removed com-

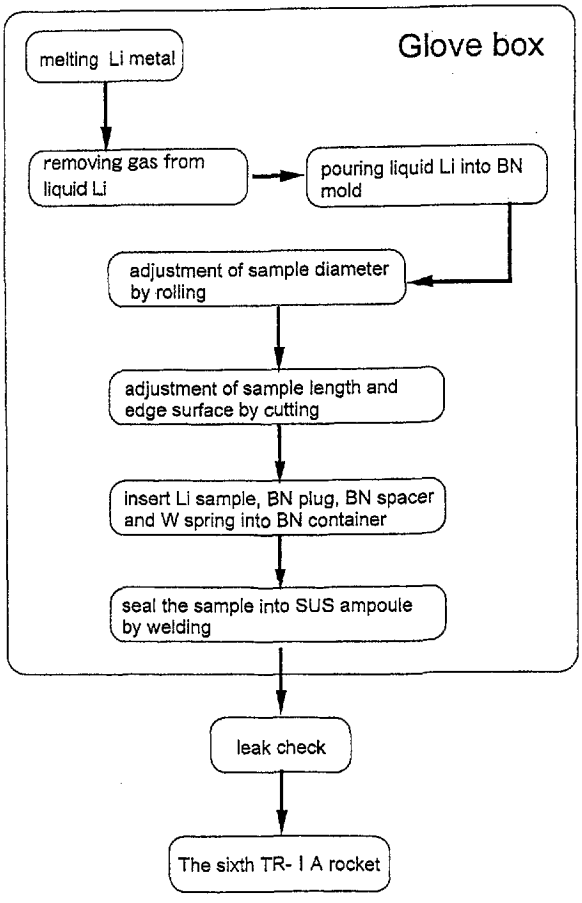

Fig. 3 The flow chart of preparation of the samples for the sixth TR-IA rocket experiment.

pletely; otherwise the concentration profile of diffusion may be spoiled by this Marangoni convection. Therefore, the slight pressure was applied to the sample by the tungsten spring throughout the course of experiment in order to prevent the formation of cavity or voids in liquid sample due to the volume change on melting and heating, keeping at holding temperature, cooling and solidification. If the force of spring is too strong liquid lithium leaks out from the clearance between outer surface of BN plug in the lithium side and inner wall of hole in BN crucible (Fig. 1). If it is too weak the cavity appears on the corner of bottom of BN crucible. The appropriate spring constant and free length of tungsten spring were determined by the volume change of sample, the clearance between outer surface of BN plug in the lithium side and inner wall of hole in BN crucible, the curvature R of the corner of bottom of BN crucible, based on the consideration of capillary (interfacial) phenomena. For this purpose the contact angle between liquid lithium and BN (crucible) material is very important. Therefore, the contact angle was measured and it was found that the spring mechanism works up to 673 K safely and over 673 K the reliability of this mechanism is lost under the present cell configuration. This determined the highest experimental temperature. In the early stage of present experiment the nitride formation causes the non-mixing of contact part between tracer rods and bars in the diffusion sample even after melting. Finally we solved this problem. However, because of the experimental schedule slightly higher temperature, 593 K, was adopted as the lowest experimental temperature for safety. To tell the truth, the contact angle measurements were performed for 13 kinds of refractory and metallic materials and only BN was appropriate for the present experiment due to its comparatively large contact angle.

The concentration of ^{6}Li and ^{7}Li was determined by the SIMS analysis. The experimental condition for the SIMS analysis was shown in **Tab. 2.**

Tab. 2 The conditions of SIMS analysis

primary ion species	O_2^+
primary ion acceleration voltage	8.0 kV
primary ion current	~400 μA
raster area	150 μm □
analytical area	30 μmϕ
degree of vacuum	~10^{-7} Pa

2.2 The method for the determination of diffusion coefficient

In the case of rocket experiment, the diffusion proceeds during the heating and cooling periods in addition to the keeping period. The contribution of heating and cooling periods can be considered by the effective time, t_{eff}, defined as follows:

$$t_{eff}=\frac{1}{D_{keep}}\int_{T_m}^{T_{keep}}\frac{D(T)}{dT/\mathrm{d}t}dT+t_{keep}$$
$$+\frac{1}{D_{keep}}\int_{T_{keep}}^{T_m}\frac{D(T)}{dT/dt}dT \qquad (1)$$

In this equation T_m is the melting temperature. Only over T_m the contribution of the atomic migration is considered to the diffusion. $D(T)$ is the diffusion coefficient as a function of temperature T. dT/dt's in the first and third terms are the heating and cooling velocities respectively. T_{keep}, D_{keep} and t_{keep} are holding temperature, diffusion coefficient at T_{keep} and holding time respectively. For the sample "type a" the following form can be used as the concentraion of tracer at time t and position x, $n(x, t)$:

$$n(x,t)=\frac{n_2-n_1}{2}\left(erf\left(\frac{d+x}{2\sqrt{Dt}}\right)\right.$$
$$\left.+erf\left(\frac{d-x}{2\sqrt{Dt}}\right)\right)+n_1. \qquad (2)$$

This solution corresponds to the case of finite depth of tracer and the solution of Fick's second law corresonding to this boundary condition has been given recently by the Laplace transformation technique[2].

For the sample "type b", the conventional solution of diffusion couple can be used.

$$n(x,t)=\frac{n_2-n_1}{2}\left(1-erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)+n_1 \quad (3)$$

Coupled equations (1) and (2) and coupled equations (1) and (3) can be solved iterative method, as already described successfully.

3. Results

The temperature profiles during the microgravity for the TR-IA-6 are shown in

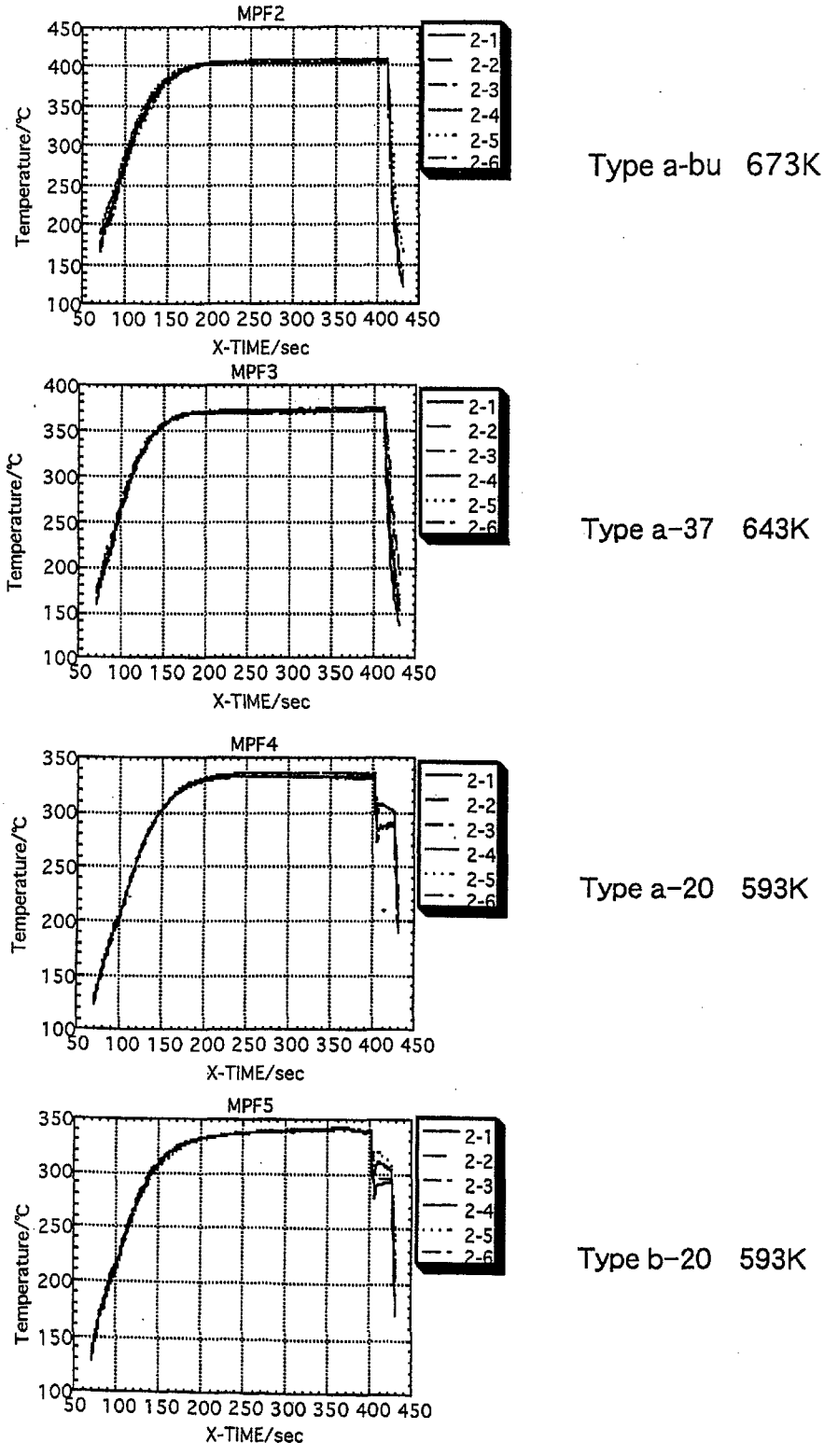

Fig. 4 The temperature pattern for the sixth TR-IA rocket experiment.

Fig. 4. The important experimental period from melting to solidification was found to be finished during the microgravity period. The holding time was 170~224 sec. The examples of concentration profiles obtained are shown in Figs. 5 and 6. In these figures dots indicate the point of experimental analysis and lines indicate the fitted curves described in Sec. 4.2. As a first look the concentration profiles seemed to be very sound in spite of very

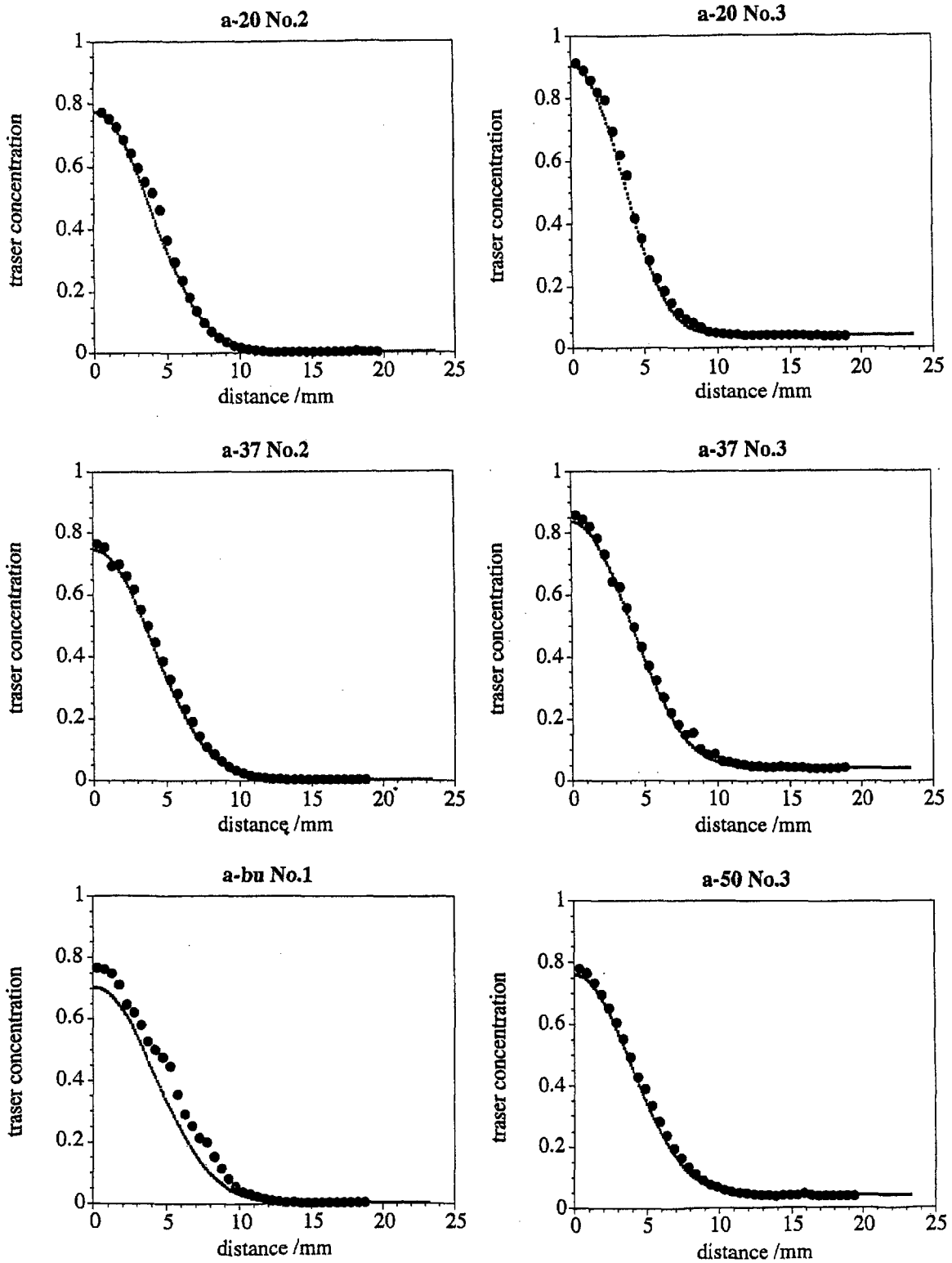

Fig. 5 The examples of concentration profiles for the sixth TR-IA rocket experiment.

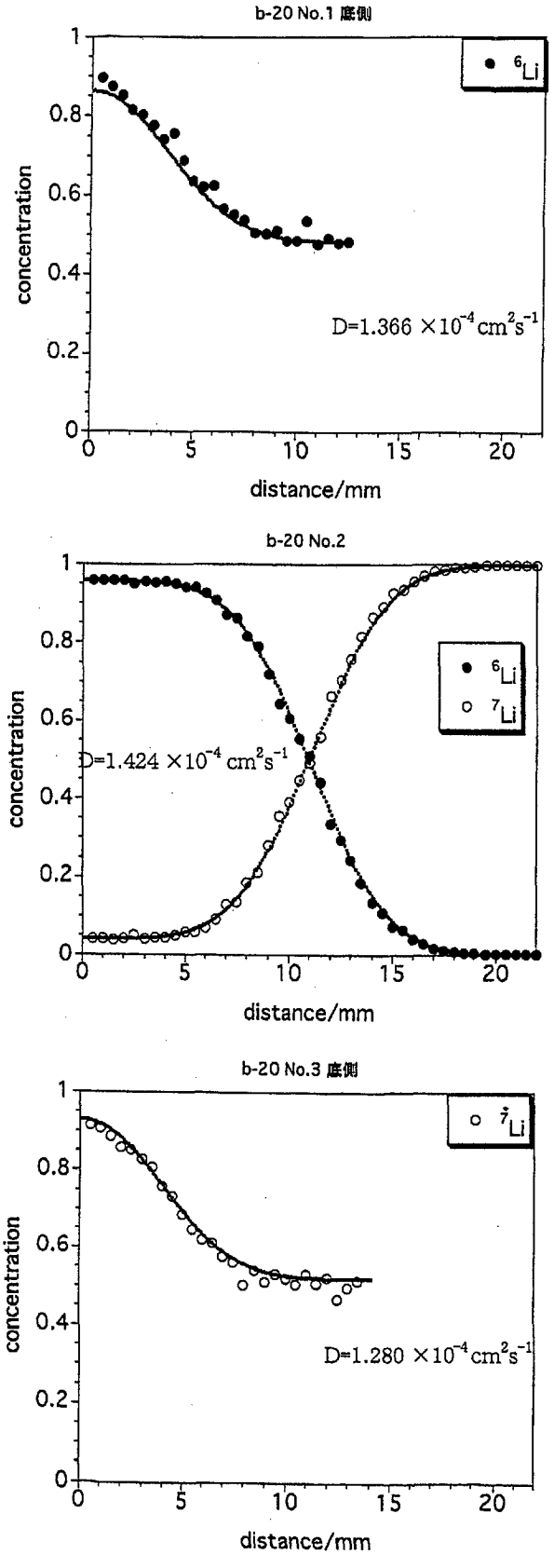

Fig. 6 The concentration profiles for b-type sample configuration at 593 K.

difficult experimental conditions due to the high reactivity of liquid lithium.

4. Discussions and Conclusions

4.1 The results of cell design

In this experiment, only for one sample among 12 total diffusion samples, the leakage of liquid lithium was found from both the bottom and plug parts of BN crucible. In addition the oxidation and the nitride formation of samples were not found on the inspection of recovered samples after the flight. Therefore in spite of very difficult experimental condition due to high reactivity of liquid lithium the fundamental technique for space experiments was successfully · acquired for very aggressive materials such as liquid lithium. In addition the tungsten spring, which was for the first time employed for space experiments, worked very well except for one case with the leakage described above.

4.2 Evaluation of diffusion coefficient

In the present rocket experiment the holding time of only about 200 seconds was retained. The contribution to the diffusion of heating and cooling periods must be taken into account. Therefore the iteration method, whose explicit procedure is shown in **Fig. 7**, was performed. The convergence of this iteration is considerably good. The diffusion coefficient was determined self-consistently by using the set of data at all experimental temperatures. The obtained diffusion coefficient is shown in **Fig. 8** for "type a" samples. The diffusion coefficient of ^{6}Li in liquid ^{7}Li is expressed as

$$D_S(^6\mathrm{Li}) = -2.49166 \times 10^{-4} + 6.64416 \times 10^{-7}\,T. \quad (4)$$

The diffusion coefficient of ^{6}Li in liquid ^{7}Li is expressed as

$$D_S(^7\mathrm{Li}) = -5.89984 \times 10^{-4} + 1.15804 \times 10^{-6}\,T. \quad (5)$$

Also for "type b" sample the quality of fitting is good. The inter-diffusion coefficient in 50 at%^{6}Li-50 at%^{7}Li was obtained to be 1.42×10^{-5} cm^{2}s^{-1} and the diffusion of ^{6}Li and ^{7}Li in liquid ^{7}Li and liquid ^{6}Li respectively are 1.37×10^{-5} cm^{2}s^{-1} and 1.28×10^{-5} cm^{2}s^{-1}. These values closely relate to Darken's

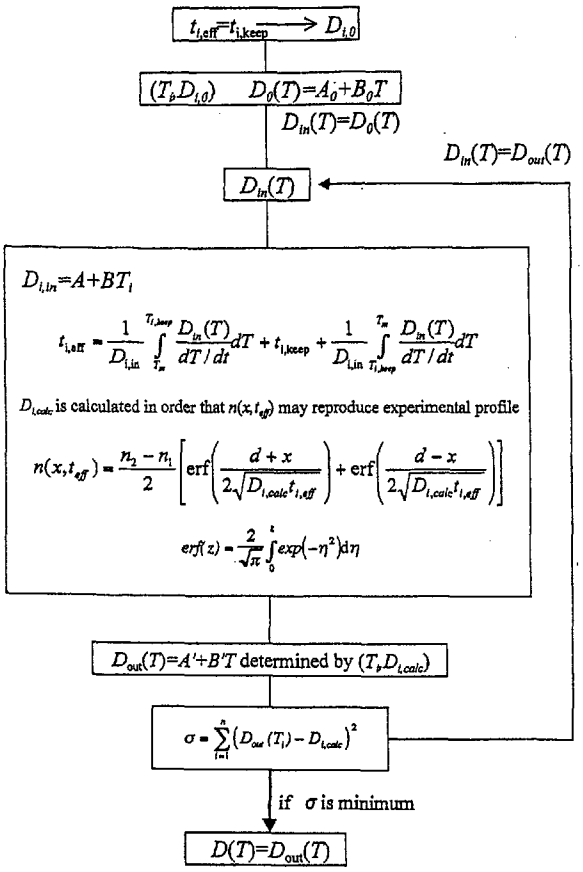

Fig. 7 The flowchart of the iteration procedure for the determination of the temperature dependence of diffusion coefficient.

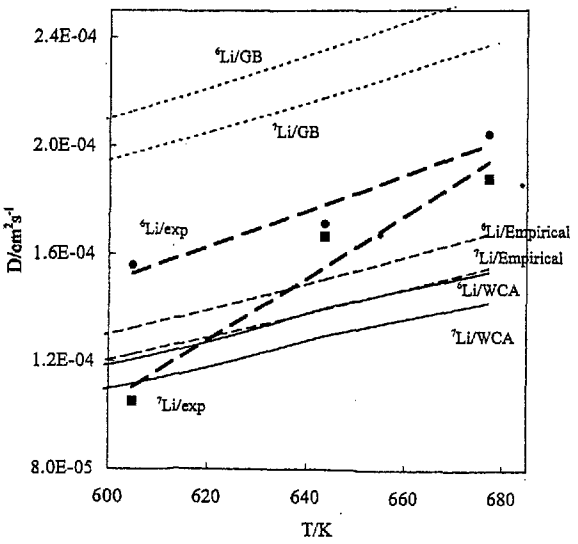

Fig. 8 Comparison of temperature dependence of diffusion coefficients of liquid Li.

relation[3]. However, Darken relation is to be fully discussed in the report of 7th TR-IA rocket experiment in 1998, in which a microgravity diffusion experiment was performed in liquid alloys, Ag-Cu.

4.3 Theoretical analysis of self-diffusion coeficient

The theoretical calculations were performed based on the hard sphere model[4]. According to this model the atomic motion of tagged atom experiences the successive binary collisions in a cage formed by the surrounding atoms. If surrounding atoms cooperatively open the path for the tagged atom, the event of diffusion occurs. The former effect was estimated by the Enskog term, D_{ENS}, and the latter effect was estimateds by the socalled back scattering factor, C_{BS}.

$$D_S^{HS}=C_{BS}D_{ENS}$$

D_{ENS}: Enskog's formula

$$D_{ENS}=\frac{3}{8}\sigma\left(\frac{k_BT}{M}\right)^{1/2}\left\{\frac{6yg_{HS}(\sigma)}{\pi}\right\}^{-1}$$

$$g_{HS}(\sigma)=\frac{4-2y}{4(1-y)^3}$$

(Pair distribution function at hard sphere diameter distance σ)

C_{BS}: Back scattering factor

$$C_{BS}=\frac{(1-y/2)^2}{(1-y)^3}\left(1-\frac{6y}{1.09\pi}\right)\left[1+\left(\frac{6y}{\pi}\right)^2\times\left\{0.4-0.83\left(\frac{6y}{\pi}\right)^2\right\}\right]$$

$$y=\frac{\pi}{6}n\sigma^3 \text{ (packing fraction)}$$

For the numerical estimations, the hard sphere diameter must be introduced into these equations. Empirical relation for the temperature dependence of the hard-sphere diameter was adopted here.

$$y=0.472 \text{ at } T_m$$

$$\frac{\sigma(T)}{\sigma(T_m)}=1.126\left\{1-0.112\left(\frac{T}{T_m}\right)^{1/2}\right\}$$

The calculated results are shown in **Fig. 8**, in which the difference of atomic mass is explicitly taken into account. Qualitatively good agreement was obtained between experiments

(exp) and calculations (Empirical).

For the hard sphere model, it is also important to adopt a proper hard sphere diameter in place of empirical one. Therefore, the hard sphere diameter was tried to be determined by the purely theoretical calculations. In this case the inter-ionic potentials required was calculated from the pseudopotential theory of metals. Thermodynamic liquid theories were applied, Gibbs-Bogoliubov liquid thermodynamic variational theory (GB) and Weeks-Chandler-Andeson liquid perturbation theory (WCA)[5]. The WCA gives slightly better results, which may be derived from the fact that the full information of inter-ionic potentials was taken into account in the case of WCA.

4.4 Isotope effects

Up to date the isotope effect, that is the effect of atomic mass difference on physical properties among same element has been studied for self-diffusion, for example, by the pulsed-field gradient NMR method[6]. In this method the self-diffusion can be measured without isotope elements. However, the strong magnetic fields are required due to the skin effects and the applicability of this method to liquid metallic system is limitted to only metallic Li practically. Therefore, this NMR method does not seems to be the main medthod for measuring the self-diffusion coefficient for metallic system. Up to date various data have been reported for the ratio of self-diffusion coefficient, $D_S(^6Li)/D_S(^7Li)$, for examples 1.18[6], 1.25[7] and 1.09[8] by this NMR method and 1.30[9] by the capillary researver technique. The molecular theories of liquids predicts the value $(7/6)1/2=1.08$. On the other hand Omini[10] estimated this ratio to be 1.25 from quantum mechanical estimation of mean free path of atoms. In the present experiment the isotope effects were tried to be detected experimentally by the long capillary method, which has been well established as the microgravity experiment. However, the accuracy of present experimental data is not sufficient, as shown in Fig. 8. The difference between $D_S(^6Li)$ and $D_S(^7Li)$ is large at some temperature and small at another temperature. The main reason for it is the very short holding time for the present experiment. Therefore, it needs more experimental improvements for accurate determination of isotope effects from the experimental side. In addition, from the theoretical side, detailed studies must be performed for the clarification of isotope effects based on the electronic theories.

Finally in this report the technique for space experiments of diffusion for very aggressive materials are successfully developed. The obtained diffusion coefficient was discussed from the microscopic atomic and electronic point of view.

Acknowledgement

T. I. is grateful to JSUP for the promotion of this experiment as the research program of Frontier cooperative Study.

References

1) H. U. Walter: "Fluid Science and Material Science in Space: European Perspective" (Springer-verlag, 1987); Feuerbacher et al., "Material Science in Space: A Contribution to the Scientific Basis of Space Processing" (Springer-verlag, 1986).
2) T. Itami, et al.: JASMA, **14** (1997) 323; ibid, **16** (1999), 79.
3) M. Shimoji and T. Itami: "Atomic Transport in Liquid Metals" (Trans Tech publications, 1986).
4) T. Itami and K. Sugimura: Phys. hem. Liquids, **29** (1995) 31.
5) T. Itami: in "Condensed Matter Disordered Solids" (ed by S. K. Srivastava and N. H. March, World Scientific, Singapore, New Jersy, London, Honkon, 1995) p. 123.
6) J. S. Murday and R. M. Cotts: Z. Naturforsch, **26a** (1971) 85.
7) A. Feinauer, G. Majar and A. Seeger: J. Phys.:Condens. Matter, **6** (1994) L355.
8) G. Krueger and W. Mueller-Warmuth: Z. Naturforsch, **26a** (1971) 94.
9) L. Loewenberg and A. Lodding: Z. Naturforsch, **22a** (1967) 2077.
10) M. Omni: Phil. Mag, **A54** (1986) 561.